

DERWENT-ACC-NO: 1970-08724R

DERWENT-WEEK: 197006

COPYRIGHT 1999 DERWENT INFORMATION LTD

TITLE: Refractory material having mo (alloy) substrate

PATENT-ASSIGNEE: TOKYO SHIBAURA ELECTRIC CO[TOKE]

PRIORITY-DATA: 1966JP-0067422 (October 15, 1966)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 70002086 B		N/A	000	N/A

ABSTRACTED-PUB-NO: JP 70002086B

BASIC-ABSTRACT:

R fractory material having Mo (alloy) substrate.. J7-. Consists: of Mo or Mo alloy substrate, Cr layer 5-40 μ in thickness coated on the Mo or alloy, Ni or Ni alloy layer of thickness 40-370 μ coated in the Cr layer, and a sprayed layer, 0.2-0.7 mm in thickness, coated on the Ni or Ni alloy layer, which essentially disperses mainly AlNi₃, Ni, NiAl, O₄, NiO, and Al₂O₃ made by the flame-spraying of composite metallic powder of Ni and Al.

Used: for constructing rockets, space machines and gas turbines. Corrosion - resistance and oxidation-resistance are good.

TITLE-TERMS: REFRACTORY MATERIAL ALLOY SUBSTRATE

DERWENT-CLASS: L02 M13

1966 JP-006742

12 A 24

昭45—

12 C 213

⑩特許公報

10 G 5

④公告 昭和45年(1)

発明の数

(全4頁)

1

2

⑤モリブデンを基体とした高温材料

⑪特 願 昭41-67422

⑫出 願 昭41(1966)10月15日

⑬発 明 者 勝田実

川崎市小向東芝町1東京芝浦電気
株式会社中央研究所内

同 吉本三則

同 所

⑭出 願 人 東京芝浦電気株式会社

川崎市堀川町72

代 表 者 土光敏夫

代 理 人 弁理士 井上一男

図面の簡単な説明

図面はこの発明に係るモリブデンを基体とした
高温材料の1実施例を説明するための1部切欠し
て示す概略縦断面図である。

発明の詳細な説明

この発明はすぐれた耐酸化性および耐食性を有
しロケット、宇宙、ガスタービンなどの構造材料
に好適するモリブデンまたはモリブデン合金を基
体とした高温材料に関する。

モリブデンの高温強度は非常にすぐれており、
とくに1000℃以上では他の耐熱金属材料の追
随を許さないがその反面モリブデンの酸化物は揮
発性のため高温における耐酸化性は非常に悪い。
また815℃付近から酸化物はとけはじめ液体の

(2). 溶射法、焼付法などによつて耐
覆する。

(3). 電着法によつて耐酸化金属を被

(4). 拡散被覆法によりモリブデン(1
酸化性物質を生成し被覆する。

(5). クラッド法により耐酸化物質を
などの被覆法が試みられているが、

によつて生成する耐酸化被覆層はい
途が限定され、高温の酸化性雰囲気

定した状態で使用するという条件に
の高温用材料としては不十分である。

かかる点に鑑みてなされたもので、
おいて耐酸化性を得ることを目的と

る。すなわちモリブデンまたはモリ
このモリブデンまたはモリブデン合

成厚さ5ないし40ミクロンのクロ
ロム層に被着された厚さ40ないし

ンのニッケルまたはニッケル合金層
ニッケルまたはニッケル合金層にニ

アルミニウムの複合金属粉末を火炎
する主としてニッケルアルミナイド

ニッケル(Ni)、4酸化アルミニウ
NiAl₂O₄)、酸化ニッケル(NiO

アルミニウム(Al₂O₃)などが実質
状態で被着された厚さ0.2ないし

溶射被覆層とからなることを特徴と
ンを基体とした高温材料である。

次に図面によつてこの発明の高温

3

4

浴温：常温 陰極：純鉛板

電流密度 10 A/dm²

処理時間 30～60秒

ついで表2に示す条件でクロム(Cr)電着層2を5～40μの厚さに形成する。クロム(Cr)を電着した表面を表3に示す条件で処理しニッケル(Ni)ないしニッケル(Ni)合金電着下地として適切な状態とする。ついで表4に示す条件でニッケル(Ni)電着層3を40～370μの厚さに形成する。

表2

CrO₃ 300 g/lH₂SO₄ 3 g/l

浴温：50～60℃ 陰極：純鉛板

電流密度 30 A/dm²

表3

(1) 脱脂

(2) 酸洗い HCl(1:1)

(3) NiCl₂・6H₂O 300 g/l

HCl(1:10) 1 l

浴温：常温 陽極：Ni板

電流密度：10 A/dm²

処理時間：120秒

表4

NiSO₄ 6H₂O 200 g/lNiCl₂ 6H₂O 45 g/lH₃BO₃ 30 g/l

浴温：45～50℃ 陽極：Ni板 P.H.5～6

電流密度 5 A/dm²

つぎに上に述べた処理によりクロム(Cr)およびニッケル(Ni)の複合層を被覆したモリブデン合金表面のニッケル(Ni)層を、12～30メッシュのアルミナ粒によつてブラスト処理し、その際生じた微細な粒子をはじめその他の異物油脂類などを溶剤を用いて充分洗滌して清浄な溶射処理

ブネル型酸化物の4酸化アルミニウム(NiAl₂O₄)、酸化アルミニウム塩型酸化物の酸化ニッケル(NiO)型酸化物の酸化アルミニウム(Al)などの諸物質4を形成することができる。

しかしモリブデン(Mo)ないし金からなる基体1の表面に電着し層2が5μ未満ではモリブデン(1)および高温におけるモリブデン(1)との強固な密着などに対する十分きないので不可である。

一方、クロム(Cr)層2が40μ・(Cr)層2の増加に伴つた性能つて不経済であるばかりでなく、部にきれつなどの欠陥が発生しやある。またクロム(Cr)層2の上にル(Ni)またはニッケル(Ni)合金未満では高温酸化性雰囲気中で長る耐酸化性が十分発揮できず、かてより消滅する事態を生ずることが一方ニッケル(Ni)またはニッケル(1370μを超えるとニッケル(Ni)合金層3の増加に伴つた性能の高温酸化性雰囲気中で長時間使用離などの欠点を生ずるおそれがある。

なおクロム(Cr)電着処理後なNi)電着処理を終了した際に要す吸蔵水素を放出させることを目的における加熱による脱水素処理を行い。また、溶射被覆層4の厚さは効果不十分であり、7mmを超なう性態の向上は認められず層間の可能性を生ずるので不可である。覆層4を生成するためのプラズマ

5

酸化性のすぐれたクロム(Cr)層2がモリブデン(Mo)の面に電着によりきわめて良好に密着し、その上に耐酸化性が優れ、酸素などの流通通路となるべきピンホールや亀裂などが存在せず適度の韌性を有し溶射被覆層を形成する主たる成分との親和力が大きく溶射被覆層が強固に付着しやすい性質を有するニッケル(Ni)層3が電着により密着し、さらにその上に溶射被覆層4が強固に付着している。溶射被覆層内においては被覆層を構成する成分のうち金属質が諸物質のバインダーの役目を果たしかつ下地を構成するニッケル(Ni)層3とよく結合する。また金属間化合物スピネル型および岩塩型酸化物は下地の金属複合層が直接燃焼炎などにさらされることを阻止し、酸素などと直接接触する機会を大幅に減少し、また腐食性を有する燃焼生成物の接触を阻止する役目を果たす。

上に述べた例においては主体のモリブデン(Mo)としてTi 0.5%、Zr 0.1%を含有するモリブデン合金を用いたが純モリブデン金属はいうまでもなく少量のジルコニウム(Zr)、チタン(Ti)、ニオブ(Nb)、バナジウム(V)、炭素(C)を含有するモリブデン合金およびモリブデン、クロム(Mo-Cr)合金についても適用できる。

また上に述べた例においては表4に示す電着条件によりニッケル(Ni)電着層を利用したがニッケル(Ni)電着層にかぎらず表5に示す電着条件で得られるニッケル、コバルト(Ni-Co)合金電着層などでも良い。また常用の手法により作製する溶射原料のニッケル、アルミニウム(Ni-Al)の複合金粉末の成分は、上に述べた成分の他に重量%でニッケル(Ni)90~55%、アルミニウム(Al)45~10%でよい。また上に述べた例に於てはプラズマ炎を使用した場合について述べたが炎の中心温度が2000℃を越えるような高温を有する酸素-アセチレン炎でもよい

6

つぎにこの発明にかかる高温材料および耐熱性試験例につき述べるモリブデン-ジルコニウム合金基板1にクロム、ニッケル(Ni)100μおよび被覆層400μを順次被覆したモリブデン-ジルコニウム合金を基体としたおよびクロム(Cr)30μ、コバルトニッケル(Co-Ni)合金層200μおよび被覆層00μを順次被覆したモリブデンを高温材料は1000℃の空气中で累計使用しても被覆層の表面はいずれも平滑さを有しなから損傷の形跡はみられなかった。また液体燃料を使用する燃焼試験によれば6回にわたる燃焼試験に耐えなから損傷は認められなかった。さらに1000℃の空气中で累計1000時間使用した高温材料の断面顕微鏡組織を調べると溶射被覆層のうち表層部のみが酸化被覆したのを認めただけで、またクロム(Cr)の一部がニッケル(Ni)層3またはニッケル(Co-Ni)合金電着層3中で顕微鏡組織にみられるクロム(Cr)が2~3割減少したのを認めただけで、

またこの発明の高温材料は単に耐酸化性に優れているというにとどまらずに耐酸化被覆層の最外層を形成している層4は金属間化合物、酸化物中に金属質(Ni)が混在しているので溶射粒子相と被覆層とにより生成する被覆層とニッケル(Ni)合金層2と強固に結合しているため酸化被覆層(Al₂O₃)、酸化ジルコニウム(ZrO₂)セラミック溶射被覆層で経年劣化による剥落などの現象は全くない。またこの高温材料の溶射被覆層4は、ブラスト処理な

特許請求の範囲

1 モリブデンまたはモリブデン合金と、このモリブデンまたはモリブデン合金に被着された厚さ5ないし40ミクロンのクロム層と、このクロム層に被着された厚さ40ないし370ミクロンの5
ニッケルまたはニッケル合金層と、このニッケルまたはニッケル合金層にニッケルおよびアルミニウムの複合金粉末を火炎溶射して生成する主としてニッケルアルミナイド($AlNi_3$)、ニッケル(Ni)、4酸化アルミニウムニッケル($NiAl_2O_4$)、10
酸化ニッケル(NiO)および酸化アルミニウム

(Al_2O_3)などが実質的に分散した厚さ0.2ないし0.7ミリからなることを特徴としたモリブデン高温材料。

引用文献

英国 特 許 8 3 1 7 8 6

金属材料 5 (5) 5 8 - 6 1
刊工業新聞社)



[19] Japan Patent Office (JP)

[12] Publication of Unexamined Patent Application (A)

[11] Japanese Patent Application Kokai Publication Number S: 45-2086

[43] The Date of Publication: January 24th 1970

Number of Inventions: 1

[52] Japan Classification: 12A 24

12 C 213

12G 5

[54] High temperature materials with a molybdenum base

Number of Pages: 4

[21] Application Number: S- 41-67422

[22] Date of Application: October 15th 1966

[72] Applicant: Toshiba Electric Inc.

Central research facility, Kawasaki city, Toshihira chou, 1

Same: [Illegible]

Address same as above

[71] Applicant: Toshiba Electric Inc.

Central research facility, Kawasaki city, [Illegible] chou, 72

[74] Representative: [Illegible]

Representative Patent Attorney: Inoe

[Simple explanation of the diagrams]

The figure is a rough vertical sectional drawing that is represented by cutting one part in order to explain an embodiment of molybdenum based high temperature material pertaining to this invention.

[Detailed Description of the Invention]

This invention pertains to molybdenum or a molybdenum alloy based high temperature material, which has superior oxidation resistance and corrosion resistance and is suitable in structural materials for rockets, space, gas turbines or the like.

Molybdenum has extremely superior strength at elevated temperature; other refractory metals do not allow [Illegible] particularly, at the temperature of more than 1000 °C, but at the same time molybdenum oxide has extremely bad oxidation resistance at elevated

temperature due to volatility. In addition, oxide starts melting at closer to 815 °C, liquid oxide coats the surface and the oxygen diffusion gradually increases through this. Oxidation multiplication of molybdenum that for example does not have an oxidation resistant plate, easily reaches 10 million times at 900-1000 °C compared to that of the nickel (Ni) alloy. Therefore, it can be said that it is impossible to use molybdenum as a sealing material in an oxidizing atmosphere.

For the purpose of enhancing oxidation resistance of molybdenum methods such as the following, namely

- (1) To add an element that will form oxidation resistance protective film.
- (2) To coat the oxidation resistant substance using the methods such as thermal spray, brazing
- (3) To coat oxidation resistant metal with an electro coat method
- (4) To generate and coat an oxidation resistant substance on the surface of molybdenum (Mo) with diffusion coating method.
- (5) To coat oxidation resistant substance with clad method.

are being attempted. However, the oxidation resistant cladding layer generated with these methods has some kind of limits with respect to applicability and is inadequate for adaptation in conditions to be used as high temperature material under stable state for long time in oxidizing atmosphere at elevated temperature.

In the view of these points, this invention aims at obtaining oxidation resistance particularly, at high temperature. In other words, a molybdenum based high temperature material characterized by and comprising of molybdenum or molybdenum alloy and a chrome layer having thickness between 5 to 40 microns that has been cladded on this molybdenum or molybdenum alloy, nickel or nickel alloy layer with thickness between 40 to 370 microns that has been cladded on this chrome layer and a spray coated layer of thickness between 0.2 to 0.7 milli that has been cladded under the state wherein, nickel aluminum (AlNi_2), nickel (Ni), nickel aluminum tetroxide (NiAl_2O_2), nickel oxide (NiO) and aluminum oxide (Al_2O_3) are primarily generated with blaze spraying of compound metal powder of nickel and aluminum on this nickel or nickel alloy layer are dispersed substantially.

Next, the first embodiment of this invention that obtains high temperature material is explained with the drawings.

First take molybdenum alloy that contains titanium (Ti) 0.5% and zirconium (Zr) 0.1%, conduct the [Illegible] process, clean the surface of molybdenum alloy and make it appropriate as chrome (Cr) electro coat base.

Table: 1

(1) Cleaning	
(2) CrO_2	300 g/_
(3) H_2SO_4	3 g/_
(4) Melting temperature:	Normal temperature, cathode: pure lead plate
(5) Current density	10 A/dm ²
(6) Process time	30-60 seconds

After that form second chrome (Cr) electro coat layer with the thickness of 5-40_ under the conditions shown in table 2.

Process the chrome electro coated surface under the conditions shown in table 3 and make it suitable as nickel or nickel alloy electro coat base. Then form the nickel electro coat layer 3 as per the conditions shown in table 4 with the thickness of 40-370_.

Table: 2

CrO ₂	300 g/ _	
H ₂ SO ₄	3 g/ _	
Melting temperature:	50-60 °C	cathode: pure lead plate
Current density	30 A/dm ²	

Table: 3

(1) Cleaning		
(2) Acid wash	HCL (1:1)	
(3) NiO ₂ 6H ₂ O	300 g/ _	
HCL (1:10)	1 _	
Melting temperature:	Normal temperature	cathode: Ni plate
Current density	10 A/dm ²	
Process time	120 seconds	

Table: 4

NiSO ₄ 6H ₂ O	200 g/ _
NiCl ₂ 6H ₂ O	45 g/ _
H ₂ BO ₂	30 g/ _

Melting temperature:	40-50 °C	cathode: Ni plate; P.H. 5-6
Current density	5A/dm ²	

Next, with alumina particles of a mesh of 12-30, perform the blast process on the nickel layer of molybdenum alloy surface that is clad with compound layers of chrome and nickel in the above described process and prepare a surface suitable for immaculate spray process by rinsing for a light minute using a solvent such as foreign grease including the fine particles generated at that time. Then, using plasma wave, spray the compound metal powder that comprised of 80% of nickel (Ni), 20% of aluminum (Al) and by including aluminum in nickel, in the thickness of 0.2-0.7 mm, coat the coat layer 4 on the surface that was blast processed.

Thus with this spray coating process, further, on the molybdenum that is coated with a compound layer consisting of chrome and nickel coat layer 4 that is comprising of all substances of nickel aluminide of intermetallic compound and metal nickel of [Illegible] cubic lattice, aluminum nickel tetroxide (NiAl₂O₄) of spinel type oxide, aluminum oxide (Al₂O₂), oxide nickel (NiO) of sodium chloride, aluminum oxide (Al₂O₂) of hematite oxide and a small amount of aluminum.

Therefore the performance is not very good since it is unable to demonstrate sufficiently firm cohesiveness of molybdenum and coating layer in nonproliferation of molybdenum

and at high temperatures, the chrome (Cr) layer 2 that has been electro coated on the base surface comprising of molybdenum (Mo) or molybdenum alloy is less than 5_

On one hand, if chrome (Cr) layer 2 exceeds 40_, not only is it uneconomical as the improvement in performance with the increase chrome layer 2 disappears but is not acceptable since the occurrence of the flaw of cracking inside chrome layer 2 can occur easily. In addition, if nickel or nickel alloy layer 3 that is to be adhered on chrome layer 2 is less than 40_, it is unable to demonstrate sufficient oxidation resistance in use for a long time at a high temperature oxidizing atmosphere and a state occurs wherein it vanishes during the blast process and hence this is unacceptable.

On one hand if nickel or nickel alloy layer 3 exceeds 370_, there is no improvement in performance following the increase in nickel or nickel alloy layer 3 and when used for longer period of time at high temperature oxidizing atmosphere the risk of a crack taking place inside a layer is there and hence is not acceptable.

Furthermore, after the chrome electro coating process, or, upon the completion of the nickel electro coating process, if [Illegible], it is preferred that dehydrogenation is performed by applying heat in vacuum to release the hydrogen that is occluded inside electro coated layer. Moreover, if the thickness of spray coat layer 4 is less than 0.2mm the effect is insufficient and if it exceeds 0.7, the possibility of crack takes place without the improvement in the performance involved in that and therefore is unacceptable. Thus, a plasma wave, in order to generate coating layer 4, can occur with wide range of arc current and arc gas flow that allows better plasma generation, but the optimal plasma is when it originates at arc current of 300-600A and arc gas flow rate of 20-40g/min, in particular.

Therefore, in the compound layer coated high temperature material that comprises of all substances including chrome and nickel of this invention composed in this manner, the coefficient of thermal expansion bears the similar value as molybdenum (Mo) and counter diffusion is difficult even at the elevated temperature; chrome layer 2 that is superior in oxidation resistance is adhered on molybdenum surface extremely well with electro coating and on that, nickel layer 3 that is superior in oxidation resistance, bears suitable [Illegible] preferably without the presence of pin hole and [illegible] with circulation path of oxygen, and possesses the property to adhere firmly on spray coating layer that has grater chemical attraction with the main component that forms the spray coat layer which is adhered with electro coating and furthermore, on top of that, spray coating layer is adhered firmly on that. Pertaining to inside spray coating, among the main components that compose the coat layer, metal substance plays the role of a binder of all substances and binds well with nickel layer 3 that comprises the base. In addition, intermetallic compounds and sodium chloride oxide prevents the base metal compound layer from exposing to direct inflammation, largely reduces the chance of direct contact with oxygen and plays a role of preventing contact with inflammable products that posses corrosiveness.

In aforementioned embodiment, as main molybdenum (Mo), molybdenum alloy containing 0.5% of Ti, 0.1% of Zr was used but it is needless to say that a pure

molybdenum metal, can also be applied in molybdenum alloy and molybdenum chrome alloy that contains small amount of zirconium (Zr), Titanium (Ti), Niobium (Nb), Vanadium (V), Carbon (C). In addition, in aforementioned embodiment, nickel electro coating layer was formed under the conditions indicated in table 4 but without restricting to nickel electro coating layer, it could also be nickel cobalt alloy electro coating layer or the like acquired under conditions shown in table 5. Moreover, the components of compound metallic powder of nickel and aluminum, which are the ingredients of the spray made by usual method, nickel could be 90-55% by weight, and aluminum 45-10% by weight other than being aforementioned components. Also in aforementioned embodiment, the usage of a plasma flame has been mentioned but it is proved that it could also be oxyacetylene that possesses flame with high temperature such that it exceeds the central temperature by more than 2000 °C .

NiSO ₂	7H ₂ O	240 g/ _
O ₀ SO ₄ H ₂ O		15 g/ _
H ₂ BO ₂		30 g/ _
NiCl ₂	6H ₂ O	45 g/ _
HOO ₃ Na		45 g/ _

Melting temperature: 54-60 °C P.H.: 4.0-4.3
 Cathode: 20% CoNi alloy plate
 Current density 5A/dm²

Next, even after using high temperature material with the base of molybdenum titanium zirconium alloy that is sequentially coated with chrome 25_, nickel 100 _ and previously mentioned spray coating layer of 400 _ on the molybdenum titanium zirconium alloy plate that has been mentioned in the test example of oxidation resistance and the heat resistance of the high temperature material pertaining to this invention and the high temperature material with the base of molybdenum titanium zirconium alloy that is sequentially coated with chrome 30_, cobalt nickel (25%O₀-Ni) alloy layer at the temperature of 1000 °C for total number of 1000 hours. No trace of damage was found on the surface of the coat layer and it had same uniformity as before using. In addition, according to the practical test attached to the combustion chamber that uses liquid fuel, even after completing 6 rounds of combustion operation, no damage was found. Furthermore, as a result of observing a cross sectional microscopic composition of the high temperature material according to this invention that was used for total number of 1000 hours under the air of 1000 °C among spray coating layers, only the superficial part was changed into monotint and one part of chrome layer 2 was [Illegible] spread into nickel layer 3 or cobalt nickel alloy electro coating layer 3 and nothing but a reduction in the thickness of chrome layer 2 that could be seen from microscope was found to be about 20-30%.

This invention does not just remain limited to the fact that the high temperature material of this invention is superior in oxidation resistance and corrosion resistance but since the spray coating layer 4 that forms the outermost layer of the oxidation resistance coat layer according to this invention, mixes metal nickel with intermetallic

compounds and oxides, and since the coat layer generated through reciprocal spray particles and spray is firmly attached to the base that is comprised by nickel or cobalt nickel alloy 3, the phenomenon of cracking and loss that were experienced in ceramic spray coating layer of aluminum oxide and zirconium oxide are absolutely not there. Moreover, since the spray coating layer 4 included in this invention can be grown easily with a spray on the metal surface that was cleaned with the blast process, if spray coating layer gets damaged after the specified time passes, spray coating layer 4 can be reproduced or mended and has the advantage that the base can be used for long time without damaging and has enhanced oxidation resistance and corrosion resistance and is also superior from economical point of view.

Furthermore, in the embodiment pertaining to this invention, the example of adhering on one surface of molybdenum base was mentioned but needless to say, this invention also applies to adhering on both surfaces.

[Scope of the Claims of The Patent]

Molybdenum based high temperature material characterized and comprising of molybdenum or molybdenum alloy and a chrome layer having thickness between 5 to 40 microns that has been cladded on this molybdenum or molybdenum alloy, nickel or nickel alloy layer with thickness between 40 to 370 microns that has been cladded on this chrome layer and a spray coated layer of thickness between 0.2 to 0.7 milli that has been cladded under the state wherein, nickel aluminum (AlNi_2), nickel (Ni), nickel aluminum tetroxide (NiAl_2O_2), nickel oxide (Ni O) and aluminum oxide (Al_2O_2) are primarily generated with blaze spraying of compound metal powder of nickel and aluminum on this nickel or nickel alloy layer are dispersed substantially.

Index of Reference literature

[Illegible] Patent: 831786

Metallic material: 5 [5] 58-61p, 1965(Daily Industrial Newspaper.)